COATINGS. ENAMELS

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GLAZES BASED ON LIQUATING GLASS COMPOSITIONS

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Liquation glazes with increased whiteness and luster have been developed. The glazes do not contain special opacifying agents. The most intense liquation phenomena in synthesized glasses are registered in the temperature interval of 950 – 1000°C. The glaze coatings obtained are recommended for use in the production of non-food household ceramics and construction ceramics.

The diversity of ceramic mixture compositions determined by a wide range of ceramic products and a variety of clays used requires glazes with various sets of properties. Ceramic products, as a rule, are coated with opacified glazes produced by introducing special opacifying agents, primarily zirconium oxide, zircon concentrate, titanium dioxide, and fluorides (fluorspar, cryolite). Opacification is produced by the formation of a finely disperse crystalline phase in firing. In this case the formation of crystals in the surface layer impairs the luster of the glaze, up to producing a dull surface texture.

The advantages of glazes opacified by phase separation in the liquid phase (liquation) include the absence of toxic and environmentally unsafe opacifiers, a few-component composition, mirror luster, and the possibility of controlling the degree of opacification of the coating. Glazes with a liquation structure represent a new variety of fritted opacified glazes that have not only good luster but increased thermal resistance, which is caused by the relatively low content of alkali and alkaline-earth metal oxides [1, 2].

However, publications on the synthesis of glasses opacified by liquation are scarce. This is due, first, to the probability of active liquation taking place at temperatures above the firing temperatures of traditional ceramics [1, 3, 4] and, second, to the low rate of the liquation process, which requires a substantial increase in the exposure duration in firing the product. In some cases glaze coatings have been obtained using expensive CeO_2 [2]. In most cases the liquation phenomena in glazes are accompanied by the formation of the crystalline phase [5 – 7].

Liquation phenomena in glazes have been studied in detail for the systems $Na_2O - CaO - B_2O_3 - SiO_2$ and $Na_2O - MgO - CaO - B_2O_3 - SiO_2$ in the range of low-alkali compositions due to their high propensity for liquation separation [3, 5]. The liquation opacificaton of glazes based on these systems was confirmed by their x-ray amorphousness. It is drop liquation or, less frequently, two-skeleton liquation.

With increasing content of Na_2O and B_2O_3 the drop size decreases and the quantity of drops per volume unit increases. In this case the degree of opacification of glasses decreases up to total refining. DTA analysis of the glasses shows the presence of two endothermic effects typical of liquating glasses: 625 – 670 and 720 – 800°C. The opacification of glasses is ensured by the capacity of bivalent cations to cause the separation of glasses into a continuous phase and a drop phase, which have different refractive indexes. The glaze has high wetting capacity. However, the de-

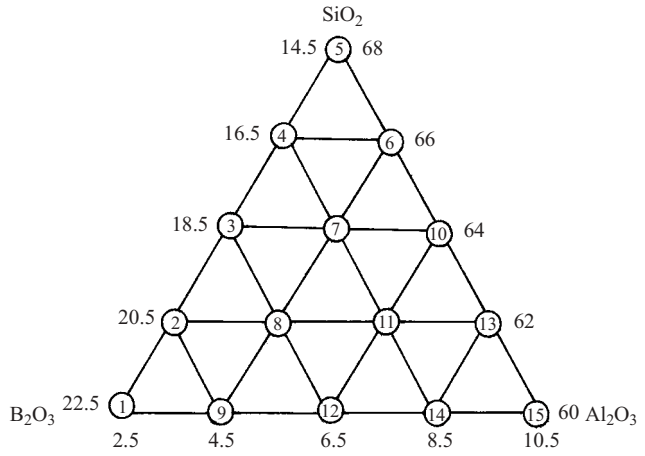

Fig. 1. Range of glass compositions (wt.%) investigated (R_2O + RO = 15%).

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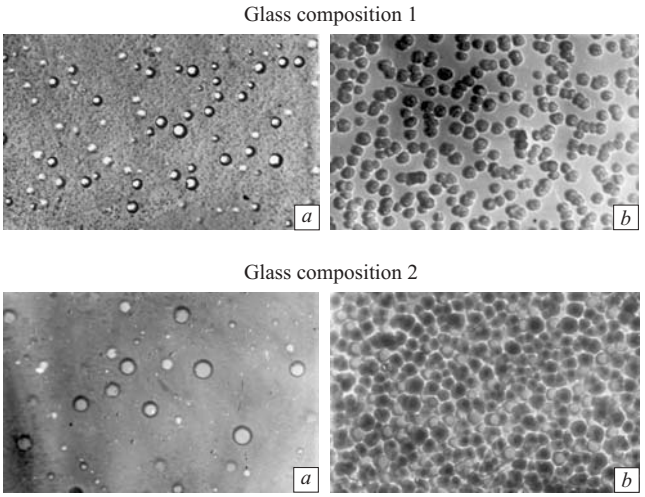

Fig. 2. Electron microscope photos of the structure of initial (*a*) and heat-treated (*b*) at 1000°C glasses.

gree of opacification is lower than that attained using special opacifiers.

In our research, glazes opacified by liquation separation were synthesized on the basis of the system B_2O_3 – Al_2O_3 – SiO_2 introducing small quantities of alkali and alkali-earth metals. The range of glass compositions considered is indicated in Fig. 1. All glasses, except for compositions 13 – 15, become well melted at a temperature of 1450°C within 1 h.

The experimental glasses were studied for their behavior under heat treatment using the gradient crystallization method, the TCLE (vertical dilatometer DKB-5A), softening temperature (method of metal rod indenting), structure (electron microscope), and phase transformations (DTA).

Heat treatment in a temperature interval of 600 – 1000°C for 1 h clearly revealed an enhanced propensity of glasses for liquation separation. The highest degree of opacification was registered in compositions 1 – 3 and 9. Within the temperature range of 950 – 1000°C the glasses became absolutely white. The studies of the glass structure with an electron microscope indicated that initial compositions 1 – 3 and 9 typically have a drop phase (15 – 20 vol.%) with a drop size of 0.1 – 0.3 μm (Fig. 2). Under heat treatment at 965°C the liquation sharply increases. The quantity of drops increases, but the drop size virtually does not change. The drop phase volume can be estimated as about 50% in glass 1 and 60 – 70% in glass 2. Thus, the optimum temperature range for the development of liquation is 965 – 1000°C.

The liquation nature of phase separation is clearly manifested on the DTA curves of glasses 1 and 2. The derivatogram reveals the presence of two endothermic effects at 640 – 650 and 730 – 735°C caused by softening in two vitreous phases. The weakly manifested exothermic effects are evidence of the low crystallization capacity of glasses.

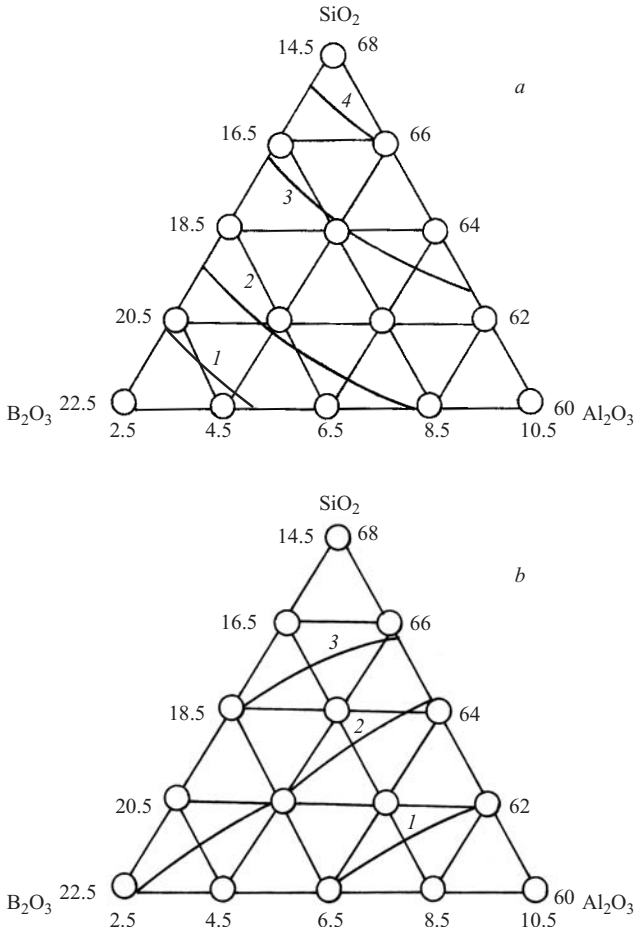

Fig. 3. Dependence of TCLE (*a*) and softening temperature (*b*) of experimental glasses on composition (R_2O + RO = 15%): *1*, *2*, *3*, and *4*) 56×10^{-7}, 58×10^{-7}, 60×10^{-7}, and 62×10^{-7} K^{-1}, respectively; *1*, *2*, and *3*) 720, 730, and 740°C, respectively.

Properties that are of special significance for glaze glasses include the TCLE and the softening temperature characterizing the degree of coordination of the TCLEs of glass and ceramics, as well as the temperature intervals of possible spreadability of glaze over a ceramic substrate.

It is notable in Fig. 3 that the TCLE decreases nonuniformly with an increasing content of B_2O_3 (transition from 62×10^{-7} – 60×10^{-7} to 58×10^{-7} – 56×10^{-7} K^{-1}). This is presumably due to the more intense development of liquation phenomena in compositions with an increased B_2O_3 composition. Furthermore, the high softening temperatures correlate with the higher-melting phase, which presumably forms the matrix component. Apparently, the lower-melting components (R_2O and RO) become concentrated in drops, whereas the matrix, in turn, in enriched with silica.

Experimental coatings were obtained on the basis of compositions 1 – 3 adding 5% refractory clay. The coatings were deposited on ceramic facing tiles with TCLE 58×10^{-7} K^{-1}. The firing of glazed tiles proceeded for 25 min within a temperature interval of 965 – 1100°C. The

TABLE 1

Composition	Firing temperature, °C	Whiteness of coating, %	Luster of coating, %
1	965	70	60
	1000	67	60
	1100	65	61
2	965	71	59
	1000	70	58
	1100	66	60
3	965	67	57
	1000	66	57
	1100	65	58

glazes had good spreadability, absence of pinholes, and a high degree of whiteness. The properties of the glaze coatings obtained are listed in Table 1.

The highest values of whiteness are registered in coatings obtained at a temperature of 965°C. An active development of liquation phenomena at this temperature sharply distinguishes the compositions considered from other known coatings with a liquation structure. As a rule, liquation in the latter evolved at higher temperatures.

A certain increase in exposure duration at 965°C (up to 40 min) increases the luster of glazes to 70%. Production of high-quality glaze coatings at 965°C makes it possible to recommend them for manufacture of household non-food ceramics (vases, flower pots, etc.) as well as for construction ceramics.

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